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# GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME XIII. TEST FOR LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROMETRY

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This document presents guidelines for a quality control program for the determination of the total lead content of gasoline within the concentration range of 0.010 to 0.10 g of lead/U.S. gals. These guidelines include:

1. Good operating practices
2. Directions on how to assess performance and quality data
3. Directions on how to identify trouble and improve data quality
4. Directions to permit design of auditing activities

The document is not a research report. It is designed for utilization by laboratory personnel.

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| Quality Control | | 14D |
| Air Pollution | | 13B |
| Gasoline | | 21D |
| Lead | | 7B |

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by

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## ABSTRACT

This document presents guidelines for a quality control program for the determination of the total lead content of gasoline within the concentration range of 0.010 to 0.10 g of lead/U.S. gals. These guidelines include:

1. Good operating practices,
2. Directions on how to assess performance and quality data,
3. Directions on how to identify trouble and improve data quality,
4. Directions to permit design of auditing activities.

This document is not a research report. It is designed for utilization by laboratory personnel.

This work was submitted in partial fulfillment of contract 68-02-1234 by Research Triangle Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of December 1974.

# SECTION I INTRODUCTION

This document presents guidelines for developing a quality assurance program for the test for lead in gasoline by atomic absorption spectrometry. For convenience of reference, this method as published by the Environmental Protection Agency in the Federal Register, July 8, 1974, is reproduced as appendix A of this report.

This document is divided into three sections.

Section I, Introduction. The Introduction lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.

Section II, Operations Manual. This manual sets forth recommended operating procedures to insure the collection of data of high quality, and instructions for performing quality control checks designed to give an indication or warning that the measurement method is out of control and that invalid data or data of poor quality are being collected, allowing for corrective action to be taken before future measurements are made.

Section III, Quality Assurance Procedures. Suggested quality control procedures, summation of the analytical method, and a statistical treatment of existing data resulting from the published analytical techniques are given. Based upon the existing knowledge of the method, quality control procedures are recommended to achieve the highest quality data for the determination of lead in gasoline by atomic absorption spectrometry.

The objectives of this quality assurance program for the method are to:

1. Minimize systematic errors (biases) and to monitor and control precision within acceptable limits in the measurement process;
2. Provide routine indications for operating purposes of satisfactory performance of personnel and/or equipment;
3. Provide for prompt detection and correction of conditions, either instrumental or operational, that contribute to the collection of poor quality data; and
4. Collect and record information necessary to describe the quality of the data.

To accomplish the above objectives a quality assurance porgram must contain the following components:

1. Recommended operating procedures,
2. Training of personnel and evaluation of performance of personnel and equipment,
3. Routine monitoring of the variables and parameters that may have a significant effect on data quality,
4. Development of statements and evidence to qualify data and detect defects, and
5. Action strategies to increase the level of precision/accuracy in the reported data.

Implementation of a properly designed quality assurance program should enable laboratory technicians to achieve and maintain an acceptable level of precision and accuracy in their testing for total lead in gasoline. It will allow a laboratory to report an estimate of the precision of its measurements for each lead analysis.

Quality assurance guidelines for the analysis of lead in gasoline by atomic absorption spectrometry as presented here are designed to insure the collection of valid data by prevention, detection, and quantification of equipment and personnel variations in the laboratory through:

1. Recommended operating procedures as a preventive measure.
2. Quality control checks for rapid detection of undesirable performance, and
3. A quality audit to verify independently the quality of the data.

The scope of this document has been purposely limited to that of a laboratory manual.

# SECTION II OPERATIONS MANUAL

## 2.0 GENERAL

This manual sets forth recommended procedures for determination of lead in gasoline by atomic absorption spectrometry. [Appendix B (Test for Lead in Gasoline by Atomic Absorption Spectrometry) is reproduced from the Federal Register, and is included as appendix A of this document.] This method is virtually identical to "Standard Method of Test for Lead in Gasoline by Atomic Absorption Spectrometry," No. 3237-73 published by the ASTM (ref. 1). Quality control procedures and checks which are designed to give an indication or warning that invalid or poor quality laboratory data are being collected, are written as part of the operating procedures and are to be performed by the operator on a routine basis. In addition, the performance of special quality control procedures and/or analysis of standard samples as prescribed by the supervisor for assurance of data quality may be required of the operator on a routine basis.

The sequence of operations to be performed for each laboratory analysis is given in figure 1. Each operation or step in the method is identified by a block. Quality checkpoints in the analysis process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines.

The precision/accuracy of data obtained from this method depends upon equipment performance and on the proficiency and conscientiousness with which the analyst performs the various steps. Detailed instructions are given for minimizing or controlling equipment error, and procedures are recommended to minimize analyst error. Before using this document, the analyst should study the method as reproduced in appendix A in detail. In addition, the analyst should study the instrument operations manual furnished by the manufacturer of the atomic absorption spectrometer. Formal instruction (training course) in the operation of an atomic absorption spectrometer is recommended for the analyst.

It is assumed that all types of apparatus satisfy the reference-method specifications and that the manufacturer's recommendations will be followed when using a particular piece of equipment.

EQUIPMENT SELECTION

1. SELECT THE EQUIPMENT ACCORDING TO THE SPECIFICATIONS GIVEN IN THE REFERENCE METHOD (APPENDIX A) AND ACCORDING TO SUBSECTION 2.1

2. PERFORM VISUAL AN. OPERATIONAL CHECKS OF EQUIPMENT AND RECORD NEW EQUIPMENT IN A RECORD FILE (2.1.1)

REAGENT PPEPARATION

3. PREPARE AND STORE REAGENTS AS DIRECTED IN SUBSECTION 2.2

CALIBRATION

4. CALIBRATE THE EQUIPMENT AND DEVELOP A WORKING ANALYTICAL CURVE ACCORDING TO SUBSECTION 2.3

SAMPLE ANALYSIS

5. IDENTIFY THE SAMPLE AND DOCUMENT ACCORDING TO SUBSECTION 2.4.1

6. ANALYZE SAMPLE ACCORDING TO SUBSECTION 2.4.3.

DATA PROCESSING

7. PLOT WORKING ANALYTICAL CURVE AND DETERMINE THE LEAD CONTENT BY READING FROM THE GRAPH ACCORDING TO SUBSECTION 2.5

8. VALIDATE DATA BY COMPARATIVE OR MEASURED VALUES OF STANDARD SOLUTION AND REFERENCE SAMPLES

9. REPORT DATA ACCORDING TO SUBSECTION 2.5

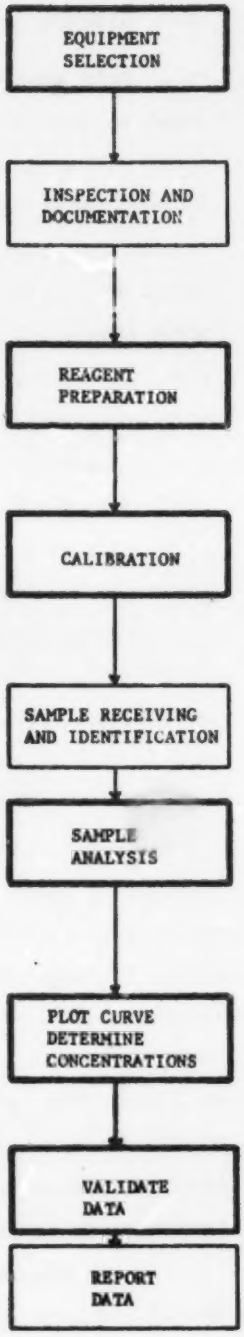


**Figure 1. Operational flow chart of the determination process.**

To conclude this introduction, let us describe the components of an atomic absorption (AA) spectrometer and the analytical determination of lead in gasoline. The basic components of an AA spectrometer are a primary source of radiation, usually a hollow cathode lamp (HCL), a method of producing neutral atoms (in this method, an air acetylene flame is utilized), a monochromator to isolate the resonant line, a detector (a photomultiplier, PM, tube), and a means of amplification and readout of the analytical signal. The basic measurement method consists of radiation from a light source (HCL) passing through the absorption medium. The neutral (ground state) atoms, $Pb^{o}$, absorb the resonant energy (2833 Å); the dispersion unit isolates the resonance line to be measured from the other lines emitted by the light source, and the resulting radiation flux is measured by the detection system. A schematic of the instrument and the absorption process are presented in figures 2 and 3, respectively.

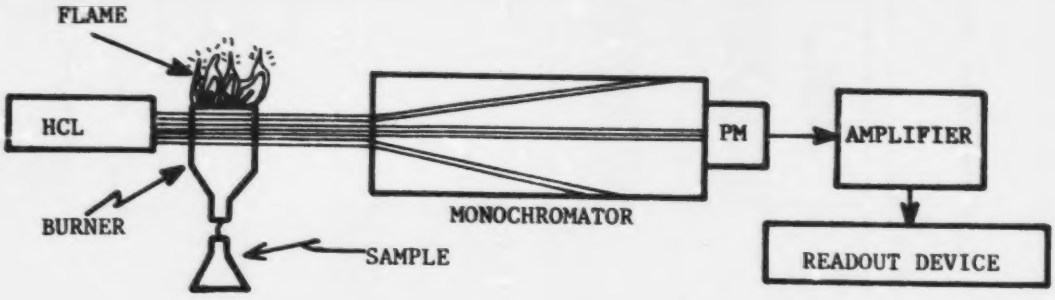


Figure 2. Basic components of an AA spectrometer.

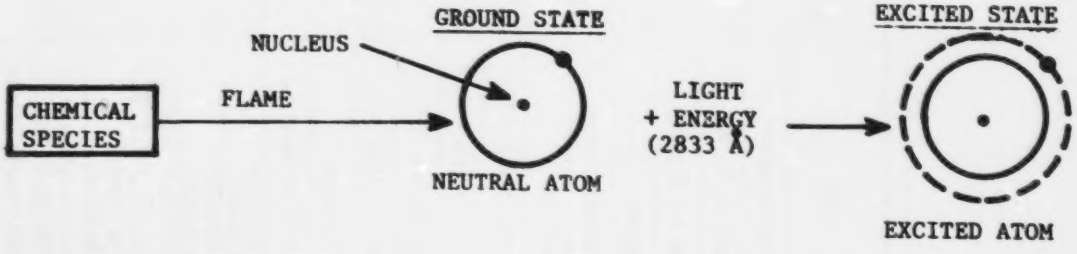


Figure 3. Absorption process.

Table 1. Lead determination checklist

LOCATION_____ LAB OPERATOR_____ DATE_____

| ITEM | EQUIPMENT (REAGENT) SOLUTION | | REAGENT PREPARATION | CALIBRATION | ANALYSIS | CALCULATIONS (Data Reporting) |
|---|---|---|---|---|---|---|
| | Receiving Record | Acceptance Check | | | | |
| 1. A.A. Spectrometer | | | | | | |
| 2. Volumetric Flasks | | | | | | |
| 3. Volumetric Pipets | | | | | | |
| 4. Micropipet | | | | | | |
| 5. Acid Wash/Solution | | | | | | |
| 6. Aliquat 336 | | | | | | |
| 7. Alq. 336 (MIBK) - 10% | | | | | | |
| 8. Alq. 336 (MIBK) - 1.0% | | | | | | |
| 9. Iodine/Toluene | | | | | | |
| 10. Iodine Solution | | | | | | |
| 11. Lead Chloride | | | | | | |
| 12. Lead Sterile Gasoline | | | | | | |
| 13. Lead Solution 5.0 g Pb/gal | | | | | | |
| 14. Lead Solution 1.0 g Pb/gal | | | | | | |
| 15. Lead/Standard Solution (0.02, 0.5, 0.1 g Pb/gal | | | | | | |
| 16. Working Standard Lead Solution | | | | | | |
| 17. Working Analytical Calibration Curve | | | | | | |
| 18. Gasoline Sample (Field) | | | | | | |
| 19. Reference Samples | | | | | | |

In the determination of lead in gasoline, the chemical pretreatment (iodine and a quaternary ammonium salt) in MIBK allows for the determination of the total lead content independent of the alkyl lead species and without sample (burner) memory effects (ref. 2).

## 2.1 EQUIPMENT SELECTION

A listing of the required apparatus along with certain miscellaneous equipment is given in table 1 in this section. Additional specifications, criteria, and/or design features as applicable are given here to aid in the selection of apparatus to insure the collection of data of consistent quality. Procedures and, where applicable, checks for acceptance limits of variability are given.

### 2.1.1 Atomic Absorption Spectrometer

2.1.1.1 Design Characteristics. The instrument used must be capable of scale expansion, nebulizer adjustment equipped with a slot burner and premix chamber for use with an air-acetylene flame. The spectrometer may be of the single-beam variety, double-beam, or dual double-beam optics. The double-beam system minimizes the effects of variation in lamp intensity, detector sensitivity, optics, and electronics. A double-beam spectrometer readily offers a stable baseline and virtually eliminates periods of stabilization when changing light sources to another element. It is also recommended that burners be adjustable on three axes. The instrument should have features for monitoring and adjustment of the burner gas-flow rates and the normal safety features to protect the operator.

Versatile burner position adjustment allows the instrument to be optimized for a particular analysis.

Note 1: Instances have been reported of the drain tube collapsing and causing flashback. It is recommended that this tube be of corrugated polytetrafluorethylene (Teflon).

For a more thorough discussion of atomic absorption spectrometers and their commercial suitability, a recent treatise such as in reference 3 should be consulted.

The wavelength mechanism should read directly in wavelength units (Å), be accurate, repeatable, and not drift with minor changes in temperature.

In general, to avoid problems when dealing with sources with complex spectra, the wavelength setting should be accurate to $\pm 2$ Å and reproducible to $\pm 1$ Å. Readout systems may be digital or an analog system with meter and recorder. A recorder gives a permanent recording of the raw data with time and offers the advantage of rechecking data. A digital system on the other hand is advantageous in handling large quantities of data.

Safety features which control the on-off sequence of the fuel and the oxidant, minimum flow rates, and ignition of the flame are recommended although they are not required to obtain a precise and accurate analysis. A good ventilation system ($\geq$ 300 $ft^3$/min) is of the utmost importance. Safety procedures in handling of cylinders, compressors, etc., must be adhered to (ref. 4).

2.1.1.2 Acceptance Check. The spectrometer should be checked out according to the manufacturer's instructions and calibrated according to the procedures in subsection 2.3.

2.1.1.3 Documentation. Record in the receiving-record log book a description of the spectrometer (basic design, single- or double-beam, etc.), its serial number, and the results of the acceptance check. Sign and date the entry.

2.1.2 Volumetric Flasks and Pipets

2.1.2.1 Design Characteristics. All glassware shall be Class A, volumetric glassware (ref. 5). An ample supply of volumetric flasks of the 50 mℓ, 100 mℓ, 250 mℓ and 1.0 ℓ sizes should be available. The following volumetric pipets are required: 2 mℓ, 5 mℓ, 10 mℓ, 20 mℓ, and 50 mℓ. It is recommended that a sufficient supply be available to perform a complete set of analyses. All pipetting should be done by a transfer device. Pipetting by mouth is not recommended under any circumstances!

2.1.2.2 Acceptance Check. The volumetric glassware is inspected for cracks, scratches, and damage and calibrated (optional) according to subsection 2.3.

2.1.2.3 Documentation. Record in the receiving-record log book a description of the glassware, its catalog or serial number, and the results of the acceptance check. Sign and date the entry.

2.1.3 Micropipet

2.1.3.1 Design Characteristics. A 100 µℓ pipet of the Eppendorf type or equivalent is required (±1 percent accuracy and reproducibility).

2.1.3.2 Acceptance Check. The micropipet is inspected for damage and checked for accuracy and reproducibility according to subsection 2.3.

2.1.3.3 Documentation. Record in the receiving-record log book a description of the pipet, its catalog or serial number, and the results of the acceptance check. Sign and date the entry.

2.1.4 Wrist Action Shaker (Optional)

2.1.4.1 Design Characteristics. A shaker (wrist action) equipped with a timer should be used.

2.1.4.2 Acceptance Check. Check performance according to manufacturer's specifications.

2.1.4.3 Documentation. Record in the receiving-record log book a description of the shaker, its serial number, and the results of the acceptance check. Sign and date the entry.

## 2.2 REAGENTS

A listing of the required reagents, along with additional specifications, criteria, and complete description of their preparation is given. In the event new reagents (new prepared solutions) are introduced during the analysis procedure, verification of the calibration curve will be considered necessary. Liquid stock standards ($PbCl_2$) will not be considered as a substitute for preparation of stock solutions from the solid-reagent-grade lead chloride.

In reagent preparation all chemicals, when available, should be ACS analytical reagent grade or better. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on analytical reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. This can be established by analysis of a quality control sample (i.e., a sample whose Pb

content is accurately known). Each lot of reagents must be checked by establishing or checking the working analytical curve before acceptance.

2.2.1 Distilled Water

Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity. It is recommended that distilled water be obtained from an all-glass distillation apparatus. Water of high purity can be obtained by distillation, followed by passing the distilled water through a mixed-bed ion exchange resin (ref. 6).

2.2.2 Acid Wash

All glassware should be washed in 1/1 (vol to vol) nitric acid-water solution prior to use in the analysis of samples. This acid wash should be followed by several rinses with distilled water.

2.2.3 Aliquat 336 (tricapryl methyl ammonium chloride)

2.2.4 Aliquat 336/MIBK Solution (10 Percent v/v)

Dissolve and dilute 100 mℓ (88.0 g) of Aliquat 336 with MIBK to one ℓ. Store in an amber bottle sealed with a polyethylene-lined cap.

2.2.5 Aliquat 336/MIBK Solution (1 Percent v/v)

Dissolve and dilute 10 mℓ (8.8 g) of Aliquat 336 with MIBK to one ℓ. Store in an amber bottle.

2.2.6 Iodine Solution

Dissolve 3.0 g iodine crystals in toluene and dilute to 100 mℓ with the same solvent. This solution should be stored in an amber (brown) bottle and sealed with a polyethylene-lined cap.

2.2.7 Lead-Sterile Gasoline

Gasoline containing less than 0.005 g Pb/gal.

2.2.8 Lead, Standard Solution (5.0 g Pb/gal.)

The analytical balance should be checked before preparing the standard lead solution by weighing a standard weight between zero and 1 g. If the measured and actual weights are within $\pm$0.4 mg, proceed with the reagent preparation. Record the actual and measured weights in the laboratory log book. If the weights differ by more than $\pm$0.4 mg, report to the lab supervisor that the balance is out of calibration. Calibration of a balance should be carried out by a certified manufacturer's representative.

Dissolve 0.4433 g of lead chloride ($PbCl_2$) previously dried at 105°C for 3 hours in approximately 200 mℓ of 10-percent liquid 336/MIBK solution (2.2.4) in a 250 mℓ volumetric flask. The transfer of $PbCl_2$ and Aliquat 336 is facilitated by a powder funnel or its equivalent. Dilute to the mark with the 10 percent Aliquat solution, mix, and store in a brown bottle having a polyethylene-lined cap. This solution contains 1,321 µg Pb/mℓ, which is equivalent to 5.0 g Pb/gal.

Note 2: In certain cases, difficulty has been experienced in dissolving the $PbCl_2$. If this problem is experienced ($\geq$ 3 hours), it is recommended that a new lot of reagent be purchased.

2.2.9 Lead, Standard Solution (1.0 g Pb/gal.)

By means of a pipet and a rubber bulb, accurately transfer 50.0 mℓ of the 5.0 g Pb/gal (2.2.8) solution to a 250-mℓ volumetric flask. Dilute to volume (to the graduation mark) with 1 percent Aliquat 336/MIBK solution. Store in a brown bottle having a polyethylene-lined cap.

2.2.10 Lead, Standard Solution (0.02, 0.05, and 0.10 g Pb/gal.)

Transfer accurately by means of pipets 2.0, 5.0, and 10.0 mℓ of the 1.0 g Pb/gal solution (2.2.9) to three 100 mℓ volumetric flasks. Add 5.0 mℓ of 1 percent Aliquat 336 solution to each flask; dilute to the mark with MIBK (2.2.11). Mix well and store in dark bottles having polyethylene-lined caps.

2.2.11 Methyl Isobutyl Ketone (MIBK)

4-methyl-2-pentanone; ACS analytical reagent grade, should be stored in its original container and kept tightly sealed.

## 2.3 CALIBRATION

A listing of the required steps for preparing the working standard solution is given in detail. A general (specific, when possible) description is rendered for the setup and calibration of an atomic absorption spectrometer. The establishment of a working analytical curve is given in a step-by-step procedure so that in later analyses one can apply a sequence of steps to determine the concentration of lead in gasoline, be it an actual field sample or a prepared standard. The working analytical curve should never be omitted or assumed to be the same for subsequent analyses.

2.3.1 Glassware Cleaning

An initial wash for all glassware should consist of a 2-hour soak in the acid wash solution, followed by several rinses with distilled water.

2.3.2 Glassware Calibration (ref. 7) (Optional)

All volumetric glassware should be freed of water streaks before being calibrated. Pipets need not be dried; volumetric flasks should be allowed to drain. The water used for calibration should be allowed to reach thermal equilibrium with its surroundings. This can be ascertained by monitoring the temperature of the water until no further change is noted. An analytical balance is used for calibrations involving volumes of 50 mℓ or less; a top-loader electronic balance is sufficient for volumes greater than 50 mℓ.

2.3.2.1 Calibration of a Volumetric Pipet. Determine the weight of a clean, dry receiver, usually a weighing bottle. Pipet an aliquot into the receiver and weigh the receiver and contents to the nearest 0.1 milligram. At 25°C the volume in mℓ delivered by the pipet is calculated by dividing the weight of the difference in the receiver's empty and full weights in grams by 0.9961 g/mℓ. (A variation of ±5°C about 25°C results in only about 0.1 percent change in the density of water.)

The calibration should be performed at least three times and averaged.

2.3.2.2 Calibration of a Volumetric Flask. Place a clean, well-drained flask on a top loader or laboratory balance and weigh to the nearest milligram. Fill the flask to the mark and weigh to the nearest milligram. Repeat this determination several times. Calculate the volume of the flask from the difference in weights divided by 0.9961 g/mℓ (average of three determinations) and etch the volume of the flask on its surface.

2.3.3 Preparation of Working Standards

At least three working standards and a blank will be prepared using the 0.02, 0.05, and 0.10 g Pb/gal standard lead solutions described in subsection 2.2.10.

2.3.3.1 Step 1. To each of four 50-mℓ volumetric flasks, the following will be added:

1. 30 mℓ of MIBK (2.2.11),
2. 5.0 mℓ of the respective low-lead standard solution--i.e., 5 mℓ of either 0.02, 0.05, or 0.10 g Pb/gal (2.2.10),
3. 5.0 mℓ of lead-free gasoline to the three working standards and to the blank. The blank will contain only 5.0 mℓ of lead-free gasoline (<0.005 g Pb/gal.),

Stopper the flasks after each addition to avoid evaporation.

2.3.3.2 Step 2. Add immediately 0.1 mℓ (100 µℓ) of iodine/toluene solution (2.2.6) by utilizing a 100 µℓ Eppendorf pipet and mix well.

Note 3: EPA practice will be to mix well by shaking vigorously for approximately 1 minute. It is suggested that this time of mixing and degree of agitation be consistent. A wrist-action shaker with timer would be advantageous for this procedure. If a shaker is used, a small piece of parafilm across the stopper will prevent the possibility of loss of sample.

2.3.3.3 Step 3. Add 5 mℓ of 1 percent Aliquat 336 solution (2.2.5) and mix.

2.3.3.4 Step 4. Dilute to the mark with MIBK and mix well. A general mixing procedure would be to invert and shake for at least 12 times. An alternative would be to employ the wrist-action shaker.

2.3.4 Preparation and Operations of an Atomic Absorption Spectrometer

The optimization of the atomic absorption instrument at 2833 Å (analytical line for determination of lead), adjustment of the gas mixture (lean blue oxidizing flame), and control of the sample aspiration rate are required for the instrument to be at optimum conditions and to give sensitivity and stability for a precise and accurate analysis (refs. 8, 9). The operation of an atomic absorption instrument should be by trained laboratory technicians who are thoroughly versed in the operation of an atomic absorption instrument. The procedure for peaking (optimization) of the monochromator at 2833 Å should be done according to the manufacturer's instructions. The control of burner position, aspiration rate, and gas mixture should be set following the manufacturer's instructions. This is only a guideline, and each spectrometer must be adjusted on an individual basis.

The instrument should be placed on a solid surface with enough work area to allow manipulation of samples during the measurement phase. The area should be free of dust and acid fumes. A vent is required to remove fumes and vapors created in the flame. This will protect the analyst, protect the instrument, and aid in stabilizing the flame.

The air supplied must be dry, and free from oil and dust. A small, oil-less air compressor with a reservoir and a gas drying unit is recommended.

Note 4: Cylinder air is required, not oxygen. Burners not specifically designed for the use of oxygen are hazardous when oxygen is used. Acetylene as supplied from the manufacturer is dissolved in acetone. Acetylene tanks should be replaced when the tank pressure is below 5 $kg/cm^2$ (71 $lb/in^2$). The tank should always be mounted vertically.

Note 5: Acetylene and copper form an explosive mixture. Copper hardware (tubing or fittings) must not be used with acetylene.

Cylinder valves must be closed to avoid the possibility of a pressure regulator failing while unattended. A regulator will always fail in the open position, thereby pressurizing the lines and creating a hazardous situation. Cylinders should be strapped down while in use and removed from the work area when empty to avoid danger to the laboratory operators.

A vessel (2-gallon capacity, wide mouth) in which the level of liquid can be observed is required to gather the effluent from the burner drain. The tip of the drain tube should always be below the level of liquid (water). The vessel should be an inert material, preferably not glass.

2.3.4.1 Optimization of Spectrometer. After installation of the instrument, a lead (Pb) hollow cathode lamp is inserted in the holder, switched on, and adjusted to the recommended current. Turn on the instrument and allow it to warm up. It is recommended that instruments, except for hollow cathode lamps, be left on continuously. Allow the hollow cathode lamp to warm at its operating current for 15 to 30 minutes. The best operating current is usually the lowest current that requires only moderate instrument gain and produces the most stability. The lamp position and the optical system are adjusted to make the light beam fall on the entrance slit of the monochrometer (in most cases, the optical system and lamps are prealigned prior to

customer delivery). The wavelength is set for the Pb line at 2833 Å by adjusting the monochrometer until a maximum response is attained.

2.3.4.2 Flame Ignition. Ignite the flame and allow the burner to reach thermal equilibrium by giving it an initial 10-minute warmup. In igniting the flame, certain rules are essential. The oxidant (air) is turned on first and the fuel ($C_2H_2$) second during ignition. Shut down requires the fuel ($C_2H_2$) to be turned off first, followed by the oxidant (air).

Using reagent blank (2.3.3.1, 2.3.3.2) adjust the gas mixture and the sample aspiration rate until a lean (blue) oxidizing flame is obtained. Do not adjust flame conditions on pure MIBK. This will result in the blank solution and subsequent analyses having an inner cone (fingers) of unburned hydrocarbons. In most cases, it is necessary to increase the oxidant (air) flow rate or to reduce the sample flow rate (aspiration rate) to obtain a sharply defined blue cone. Failure to follow this procedure can result in poor precision.

2.3.4.3 Burner Adjustment. While aspirating the 0.10 g Pb/gal working standard (2.3.3.1, 2.3.3.2), adjust burner height for maximum absorption. Also adjust the burner forward and back to achieve maximum sensitivity. Some instruments require the use of scale expansion to produce a response of 0.150 to 0.170 absorbance for the 0.10 g Pb/gal standard. If an instrument requires scale expansion, the 0.10 g Pb/gal standard should be adjusted to read 0.150 absorbance units.

2.3.4.4 Development of a Working Curve.

Step 1. Aspirate the reagent blank (2.3.3.1, 2.3.3.2) and adjust the instrument to read zero absorbance.

Step 2. Aspirate the three working standards. The blank should be aspirated after each standard.

Step 3. Check for linearity. For example, if the 0.10 g Pb/gal standard reads 0.150 absorbance units then the 0.05 and 0.02 standards should read 0.075 and 0.030 absorbance units, respectively (fig. 4).

Step 4. A working calibration curve should be prepared with absorbance plotted versus the three working standard concentrations (fig. 4). The curve should be linear within this concentration range. If a linear curve is not obtained, additional working standards between 0.01 and 0.10 g Pb/gal

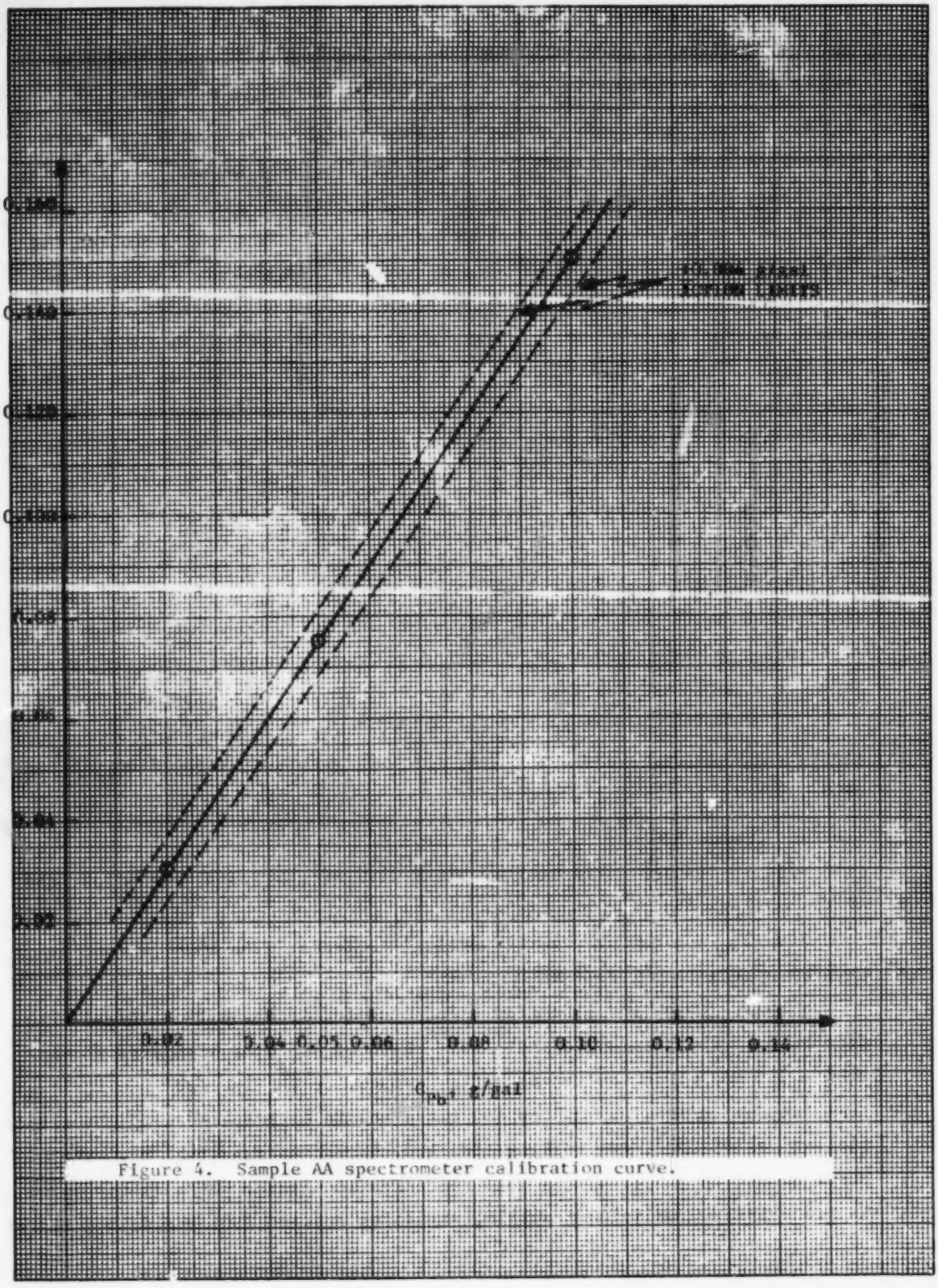


Figure 4. Sample AA spectrometer calibration curve.

should be prepared by appropriate dilutions according to this section (2.3.3.1, 2.3.3.2). If the problem is ascertained to be instrumental, the instrument must be repaired. (Data points deviating more than about ±0.002 g Pb/gal from the best-fit curve should not be expected.) Chemical standards and new reagents should be prepared, and the working analytical curve repeated before calling the instrument manufacturer.

## 2.4 SAMPLE ANALYSIS

A listing of the required steps in sample analysis is given. Sample documentation, including receiving and analysis, in the laboratory are rendered to prevent confusion and loss of identity of the sample. Sample handling procedures are recommended to prevent unwanted bias in the method.

### 2.4.1 Recommended Quality Control Practices

As part of the analysis procedures, certain checks are recommended for quality control and for data-quality-assessment purposes. Procedures for performing the checks are given along with recommendations for a minimum acceptable frequency for performing the checks. If the checks indicate problems in the analysis of gasoline samples, the frequency of the checks should be increased until the problem is identified and corrective action taken.

To aid in understanding the following discussion, five types of samples referred to in the analysis procedure are defined here. They are:

1. Gasoline sample: A gasoline sample collected in the field for analysis of its Pb content,
2. Blank sample: A working standard sample containing 5.0 mℓ of lead-free gasoline (< 0.005 g Pb/gal) and no standard lead solution (see 2.3.3.1) used to establish the baseline for the AA spectrometer.
3. Standard reference sample (SRS): A gasoline sample taken from a stock of gasoline the Pb content of which has been certified by the NBS or other suitable agencies such as the Quality Assurance and Environmental Monitoring Laboratory of the EPA. An SRS can serve as a quality control sample when its concentration is known by the analyst. However, its primary use will be as a blind

sample (i.e., the analyst does not know the concentration) for performance audits,

4. Quality control sample: A gasoline sample for which the Pb content is known to the analyst and analyzed periodically for quality-control purposes. Preferably this would be an SRS; however, if such samples are not available, duplicate results from gasoline samples can be used.
5. Working standard samples: Samples prepared by the analyst from stock reagents and used as calibration standards.

The following sequence of analyses is recommended as the minimum level acceptable for quality control and data-quality-assessment purposes.

1. The spectrometer calibration curve should be verified by analyzing the working standard samples a) before analyzing gasoline samples, b) at the end of a 4-hour working period or at the end of a measurement cycle if less than 4 hours. If all points fall within the $\pm$0.004 g Pb/gal limits given in figure 4 and are randomly distributed about the curve, the calibration is acceptable. If any point falls outside the limits, the calibration curve should be reconstructed before continuing. Reanalysis of gasoline samples is necessary when the results of the previous analysis combined with the apparent drift of the spectrometer indicate that the actual Pb content in the samples could be near the standard: i.e., 0.05 g Pb/gal.
2. Every tenth sample analyzed should be a quality-control sample. If SRS's are available for this purpose the results should be plotted on a control chart as illustrated in figure 8. (Note the action limit of $\pm$0.005 g Pb/gal can be used until sufficient data are obtained (e.g., 20 to 30 measurements) to compute new limits which should be less than those for duplicates.) Otherwise, a second aliquot should be taken from the first, eleventh, twenty-first---gasoline samples and analyzed as the tenth, twentieth, and thirtieth---gasoline samples respectively. Results should be plotted on a control chart as directed in 3.2.1.
3. A blind sample (i.e., an SRS provided by the supervisor) should be analyzed a) after every 20 gasoline samples or for every

measurement cycle if less than 20 samples are to be analyzed, and

b) any time a gasoline sample is found to exceed the standard.

2.4.1 Sample Receiving Procedure

Samples as received from the field must be labeled with at least the following information:

1. Time of station test,
2. Date of station test,
3. Location,
4. Sample number,
5. Inspector name and title,
6. Inspector signature.

This data should be recorded in a sample receiving log book as shown in figure 5. At this time, each sample should be assigned a laboratory analysis number. This should be recorded in the sample receiving log book and on the chain-of-custody label.

2.4.3 Sample Handling Procedures

The samples should be handled and stored in accordance with safety procedures for flammable liquids. Since light fractions of a gasoline sample evaporate easily, it is recommended that the sample be stored under refrigeration. Before analysis, the sample should reach room temperature. The sample must be tightly covered at all times except when removing aliquots for analysis.

2.4.4 Analysis Procedure

Step 1. For each gasoline working standard sample, or SRS sample, transfer 30 mℓ MIBK into a 50 mℓ volumetric flask and add 5.0 mℓ (pipet with rubber bulb or equivalent transfer device) of the sample and mix. The gasoline should be allowed to reach room temperature (25°C) before the aliquot is removed.

Step 2. Refer to subsection 2.3 and perform the analysis according to (2.3.3.2-2.3.3.4).

Step 3. Aspirate (suction capillary is immersed in the solution) the samples and working standards (2.3), and record the absorbance values with frequent checks of the zero. It is recommended that the blank be aspirated

SAMPLE RECEIVING RECORD

1. Test Station Sample Identification

Test Station Sample Number:

Test Station Location:

Region:

Date of Station Test: ___/___/___
MO DA YR

Time of Station Test: ___:___
HR MIN

Inspector's Name:

Inspector's Title:

2. Laboratory Identification

Laboratory Name:

Laboratory Address:

Laboratory Analysis Number:

3. Laboratory Technician

Name:

Signature:

Date:

Figure 5. Sample receiving record.

between each sample. It is recommended that the quality-control procedures given in section 2.4.1 be followed during the analysis of samples.

During the course of analysis (measurement phase), difficulties may arise. An indication of problems can be detected by changes in absorbance of the blank and/or a standard sample (working standard). Another recommended check is to analyze an SRS with known concentration for every 10 gasoline samples or to aspirate the initial tenth gasoline sample with each succeeding group of 10 samples. If the absorbance is low and unsteady, the atomizer may be blocked. The atomizer must then be cleaned or replaced. If the flame looks unsteady or colored when spraying the blank, the burner should be cleaned. The instrument operation manual (manufacturer) should be consulted for cleaning procedures.

The standard solutions (working analytical curve) should be aspirated at the end of a 4-hour work period or at the end of each measurement cycle.

## 2.5 CALCULATIONS AND DATA REPORTING

Plot the absorbance values versus concentrations for the working standards as illustrated in figure 4. Determine the concentrations of the samples from the calibration curve by reading the g Pb/gal corresponding to the sample absorbance. The calculations are complete when the calibration data record, shown in figure 6, is recorded in the laboratory test record log book.

Concentrations of lead should be reported to the nearest 0.001 g Pb/gal. The total lead in gasoline is to be recorded in the laboratory test record log book in the format shown in figure 7. The data report is not complete until the laboratory test record is filled out.

**CALCULATION DATA RECORD**

1. **Test Station Sample Identification**

   **Test Station Sample Number:**

   **Region:**

   **Date of Station Test:** ___ / ___ / ___
   Mo Da Yr

   **Time of Station Test:** ___ / ___
   Hr Min

2. **Laboratory Identification**

   **Laboratory Name:**

   **Laboratory Address:**

   **Laboratory Analysis Number:**

3. **Calculation Data**

   Lead Calibration Curve Graph Number:

   **Absorbance of the Sample:**

   **Absorbance of the Blank:**

   Grams of Lead Read from Calibration Curve:

   **Milliliters of Gasoline Sample:**

   **Temperature of Gasoline Sample:**

4. **Test Information**

   **Date of Laboratory Test:** ___ / ___ / ___
   Mo Da Yr

   **Time of Laboratory Test:** ___ / ___
   Hr Min

   Pb, g/gal:

5. **Laboratory Technician**

   **Name:**

   **Signature:**

Figure 6. Calculation data record.

LABORATORY TEST RECORD

1. Test Station Sample Identification

Test Station Sample Number:

Region:

Date of Station Test: ___/___/___
MO DA YR

Time of Station Test: ___:___
HR MIN

2. Laboratory Identification

Laboratory Name:

Laboratory Address:

Laboratory Analysis Number:

3. Test Information

Date of Lab Test: ___/___/___
MO DA YR

Time of Lab Test: ___:___
HR MIN

Pb, g/gal

4. Laboratory Technician

Name:

Signature:

Date:

Figure 7. Laboratory test record.

# SECTION III QUALITY ASSURANCE PROCEDURES

## 3.0 GENERAL

The control of data quality is a function of two related activities of the quality assurance program: 1) development of standard operating procedures including control limits, and 2) assurance of conformance to the procedures and control limits. Standard operating procedures and control limits are recommended in the operations manual of this document. It is emphasized that if the analyst conscientiously adheres to the procedures and checks of section II, then the precision and accuracy of the lead determinations should be within acceptable limits. Assurance of data quality basically involves collecting the information necessary to document and demonstrate the quality of the measured data. This section of the document will discuss the activities necessary to document and demonstrate data quality.

Verification of data quality is important in this instance because the data generated by this method are to be used to determine if the standard for lead in gasoline is being exceeded. If results indicate that the standard is being exceeded, the appropriate enforcement group will be required to take action. Thus, the professional competence of the analyst, the operating procedures used, and the measured values that he reports may be challenged in a court of law.

The quality assurance procedures presented in this section should be carried out or closely monitored by the individual directly responsible for the quality of the reported data. In each laboratory, one individual should be assigned the responsibility for quality assurance. With the exception of the independent audit, all functions could be performed by the analyst if properly trained.

The purposes of this section are to:

1. Present information relative to the measurement method (i.e., a functional analysis) to identify the important operations and factors,
2. Present techniques for the collection of information to identify trouble,

3. Present an independent performance audit procedure for use in quantifying data quality on an interlaboratory basis,

4. Present techniques for data-quality assessment.

These four purposes will be discussed in the order stated in the subsections that follow. The first subsection (3.1) will contain a functional analysis of the measurement method with the objective of identifying the most important factors that affect the quality of the reported data and of estimating the expected variation and biases in the measurements resulting from equipment and analyst errors.

Subsection 3.2 will contain suggestions for the collection and analysis of information to identify trouble. This will involve the use of control charts for duplicate measurements of gasoline samples and for measurement of working standard samples with appropriate criteria for decision-making concerning whether the operation is in control and should be left alone or if it is out of control and corrective action required.

Subsection 3.3 contains a discussion of an independent performance audit. Such an audit involves randomly inserting standard reference samples (i.e., NBS or otherwise certified samples) into the measurement process. Such an audit, if feasible, could serve as an independent check of the measurement process from sample handling through the final calculations. It would provide a means of assessing data quality as a function of bias and precision and serve as an independent verification of data quality for future users of the data.

Data quality assessment is discussed in subsection 3.4. A method for estimating the precision and accuracy of the reported data using the results from the independent performance audit is given. Also, a method of testing the quality against given standards using sampling by variables is given.

## 3.1 FUNCTIONAL ANALYSIS OF THE MEASUREMENT METHOD

The determination of lead in gasoline requires a sequence of operations and measurements that yields as an end result a number that serves to represent the mass of lead in a unit volume of gasoline. The degree of agreement between the measured and the true value of a sample can be estimated from the agreement between measured and known or accepted values of reference samples. Precision and accuracy of the measurement process are reduced to

and/or maintained within acceptable limits by identifying and, where feasible, by eliminating systematic errors. The importance of a variable on the precision and/or accuracy of a measurement process is a function of the variable's mean value and variance, how it is related to the dependent variable, and its probability of occurance under normal operating conditions.

The objectives of this subsection are to:

1. Evaluate variables and estimate error ranges,
2. Determine through a variance analysis the expected variability in the lead in gasoline measurements,
3. Estimate through a bias analysis the expected bias, if any, in lead in gasoline measurements.

A functional analysis of the measurement process is performed to determine all the major operations and variables that may affect the quality of the reported measurements. Data quality is characterized by measures of precision and bias. In subsection 3.1.1, variables believed to be important to the measurement method are discussed. Estimates of the mean, variance, and probability distribution are made using data from published reports when available, and using engineering judgments when documented data are not available. These data are then used in a variance analysis (subsection 3.1.2) to determine the resulting variability of the measured value, i.e., the mass of lead per unit volume of gasoline. The data from subsection 3.1.1 are also used in subsection 3.1.3 to estimate the potential bias of the measurement process.

### 3.1.1 Variables Evaluation and Error Range Estimates

A sample, at the time it is collected, will contain a specific but unknown quantity of lead per unit volume of gasoline. The difference in the lead-per-volume ratio existing at the time of sample collection and that measured at some latter time is due to errors in the measurement process. Following a hypothetical sample of gasoline from collection through analysis, the following operations could, if not properly carried out, adversely influence the measurement results.

1. Sample handling. Exposure to the atmosphere at any time between sample collection and analysis could result in the loss of the light fractions of the gasoline sample due to evaporation. This

would effectively increase the lead content per unit volume, resulting in a higher-than-true measured value.

2. Failure to properly tune the instrument. Failure to use a definitely lean (oxidizing) flame can reduce the precision of the measurement method. The flame should be adjusted to give a sharply defined blue cone with no trace of unburned hydrocarbons visible above the cone.
3. Preparation of standards. Preparation of standards from weighing of dried reagent-grade lead chloride through the dilutions required to obtain the standard solutions could be a source of errors if careful technique is not followed.

The above operations are rated 40, 40, and 20 for their contribution to the measurement-method variability. This rating is an estimate and not derived from actual data.

Sample handling would act as a positive bias and would probably be randomly distributed on a between-laboratories basis. It would then be expected to have a greater influence on the reproducibility of the method where several laboratories are involved than on the repeatability where only one laboratory is involved. Using the values of $\sigma_r$, the repeatability standard deviation, and $\sigma_R$, the reproducibility standard deviation, as obtained in subsection 3.1.2 and, assuming that sample handling accounts for 40 percent of the total variance, the error term for sample handling (SH), will be modeled as a normal variate with a mean of 0.001 g Pb/gal and standard deviations of 0.0014 g Pb/gal for repeatability and 0.0023 g Pb/gal for reproducibility. These will be written as N(0.001, 0.0014) and N(0.001, 0.0023) for repeatability and reproducibility respectively.

There are no actual measurement data to support the positive mean value. However, it is felt that, in general, evaporation and sample contamination combined will result in a positive bias.

Failure to properly tune the instrument (i.e., to properly adjust the flame) will result in reducing the precision of the measurement method. The error due to flame adjustment (FA) would be expected to be positive, especially with gasoline that has a high aromatic content. It is therefore modeled by a normal distribution with a mean of 0.001 g Pb/gal and standard

deviations of 0.0014 g Pb/gal and 0.0023 g Pb/gal for repeatability and reproducibility, respectively.

Variability in the Preparation of Standards (PS) is assumed to account for only 20 percent of the total variability. On a reproducibility bases, the purity of the reagent-grade lead chloride, the accuracy of weighing out 0.4433 g of the reagent, and subsequent dilutions to obtain the required standard solutions are sources of error. For repeatability the variability of the standards should be very small. The error due to preparation of standards is modeled as N(0, 0.0008 g Pb/gal) and N(0, 0.0016 g Pb/gal) for repeatability and reproducibility respectively.

Table 2 summarizes the error sources discussed above with their estimated mean values and standard deviations.

Table 2. Estimate means and standard deviations of important error sources

| Operation | Repeatability | | Reproducibility | |
|---|---|---|---|---|
| | Mean (g Pb/gal) | Std. dev. (g Pb/gal) | Mean (g Pb/gal) | Std. dev. (g Pb/gal) |
| Sample Handling (SH) | 0.001 | 0.0014 | 0.001 | 0.0023 |
| Instrument tune up (FA) (Flame Adjustment) | 0.001 | 0.0014 | 0.001 | 0.0023 |
| Preparation of Standards (PS) | 0.0 | 0.0008 | 0.0 | 0.0016 |

3.1.2 Variance Analysis

Many different factors may contribute to the variability of a measurement method, for example:

1. The analyst,
2. Apparatus and reagents used,
3. Equipment calibration,
4. The environment (temperature, humidity, pollutant concentration, etc.).

The variability will be larger when the measurements to be compared are performed by different analysts and/or with different equipment, than when they are carried out by a single analyst using the same equipment. Many

different measures of variability are conceivable according to the circumstances under which the measurements are performed.

Only two extreme situations will be discussed here. They are:

1. Repeatability, r, is the value below which the absolute difference between duplicate results, i.e., two measurements made on the same sample by the same analyst using the same equipment over a short interval of time, may be expected to fall with a 95 percent probability.
2. Reproducibility, R, is the value below which the absolute difference between two measurements made on the same sample by different analysts in different laboratories using different equipment may be expected to fall with a 95 percent probability.

The above definitions are based on a statistical model according to which each measurement is the sum of three components:

$$C_{Pb} = \bar{C}_{Pb} + b + e \qquad (1)$$

where

$C_{Pb}$ = the measured concentration of Pb in gasoline, g Pb/gal

$\bar{C}_{Pb}$ = the general average, g Pb/gal

b = an error representing the differences between laboratories, g Pb/gal.

e = a random error occurring in each measurement, g Pb/gal.

In general b can be considered as the sum

$$b = b_r + b_s \qquad (2)$$

where $b_r$ is a random component and $b_s$ a systematic component. The term b is considered to be constant during any series of measurements performed under repeatability conditions, but to behave as a random variate in a series of measurements performed under reproducibility conditions. Its variance will be denoted as

$$\text{var } b = \sigma_L^2, \qquad (3)$$

the between-laboratory variance including the between-analyst and between-equipment variabilities.

The term e represent a random error occurring in each measurement. Its variance

$$\text{var } e = \sigma_r^2$$

will be called the repeatability variance.

For the above model the repeatability, r, and the reproducibility, R, are given by

$$r = 1.96\sqrt{2}\,\sigma_r = 2.77\,\sigma_r \tag{4}$$

$$R = 2.77\sqrt{\sigma_r^2 + \sigma_L^2} = 2.77\,\sigma_R. \tag{5}$$

where $\sigma_R^2$ will be referred to as the reproducibility variance.

Values of $\sigma_r$ and $\sigma_R$ can be obtained from the values of repeatability and reproducibility respectively as given for the reference method in the Federal Register (see appendix A). The repeatability, r, is given as 0.005 g Pb/gal. Using this value in equation (4) gives $\sigma_r = 0.0018$ g Pb/gal. Reproducibility is given as R = 0.01 g Pb/gal; then from equation (5) $\sigma_R$ = 0.0036 g Pb/gal.

As can be seen the reproducibility standard deviation is larger by almost a factor of 2 than the repeatability standard deviation. It is felt this large difference is due primarily to differences in analyst techniques for performing operations such as sample handling, proper flame adjustment, and preparation of standards.

For this analysis it is assumed that the total variance is equal to the sum of the variances of the three operations previously discussed. The variance (see table 2) of $C_{Pb}$ then is given by

$$\sigma^2\{C_{Pb}\} = \sigma^2\{SH\} + \sigma^2\{FA\} + \sigma^2\{PS\}. \tag{6}$$

Using the relationship in equation (5) the between-laboratory variance $\sigma_L^2$ can be determined.

$$\sigma_L^2 = \sigma_R^2 - \sigma_r^2$$

and $\sigma_L = 0.0031$ g Pb/gal.

### 3.1.3 Bias Analysis

There are no data available for estimating the bias of the measurement process. However, the assumption made concerning instrument tune up in the previous subsection would result in a positive bias of about 4 percent at $C_{Pb} = 0.05$ g Pb/gal. The assumption concerning bias could be evaluated by measuring reference samples, if and when they become available.

Assuming that the true or acceptable value, $C'_{Pb}$, of a gasoline sample is known then from equation (1)

$$\bar{C}_{Pb} - C'_{Pb} = \hat{\tau} \qquad (7)$$

represents an estimate of the bias of the measurement method. An estimate of the bias can be obtained from audit results as discussed in section 3.3.

## 3.2 COLLECTION OF INFORMATION TO IDENTIFY TROUBLE

In a quality assurance program, one of the most effective means of preventing trouble is to respond immediately to indications of suspicious data or equipment malfunctions. Certain visual and operational checks can be performed by the analyst while the measurements are being made to help insure the generation of data of acceptable quality. These checks are written as part of the routine operating procedures in section II.

The use of control charts is recommended as a method for monitoring and documenting the performance level of the measurement process. Recommended control charts are:

1. A control chart for duplicate results (or measurements of SRS's) to monitor analyst technique and equipment stability.
2. A control chart for the measurement of working standard solutions to monitor calibration stability.

A sample control chart for each of the above parameters with suggested limits is given in the following subsections. Control charts are discussed in textbooks such as references 10 and 11.

### 3.2.1 Control Chart for Duplicates

A sample control chart for the difference in duplicate measurements of a gasoline sample is given in figure 8. It is recommended that a duplicate measurement be made on every tenth sample (e.g., sample number 1 would be reanalyzed as sample number 11, and sample number 10 reanalyzed as sample number 21). The second measurement should be separated by at least 9 samples from the original measurement.

From control chart theory, the average range, $\bar{R}$, for duplicates is equal to 1.128 x $\sigma_r$, or 0.002 in this case. The upper control limit, UCL, is equal to 3.27 $\bar{R}$ or 0.0065 as shown in figure 8. (Note that this is the 3-sigma value, whereas reproducibility was defined as the 2-sigma value.)

Take the absolute difference in the duplicates, and plot the point on the graph of figure 8. Connect each point to the previously plotted point by a straight line. A point falling outside the UCL indicates that an actual change has occurred in the measurement process. Such a change could be due to poor technique, equipment change, and/or sample deterioration. As long as the plotted points remain within the UCL, the measurement process is considered in control, and no action is required.

When a point falls outside the UCL, a quick check would be to prepare and measure a working standard sample of about the same absorbance to check the calibration curve. If the calibration curve has not changed, the most likely cause of the excess variability is poor technique. The sample (another aliquot from the same gasoline sample or SRS) should be measured again after reviewing the analysis procedures. Plot the difference in the original and third measurements and, if it is below the UCL, continue the operation. Document the cause and corrective action taken on the control chart of figure 8.

### 3.2.2 Control Chart for Working Standard Samples

Duplicate measurements of a standard sample should agree closer than duplicate measurements of a gasoline sample, because a portion of variability due to analyst technique is eliminated. It is estimated that the calibration curve should be suspect if the measured value of a standard sample differs more than 0.004 g Pb/gal from its known value.

Figure 9 is a sample control chart for the differences in the measured

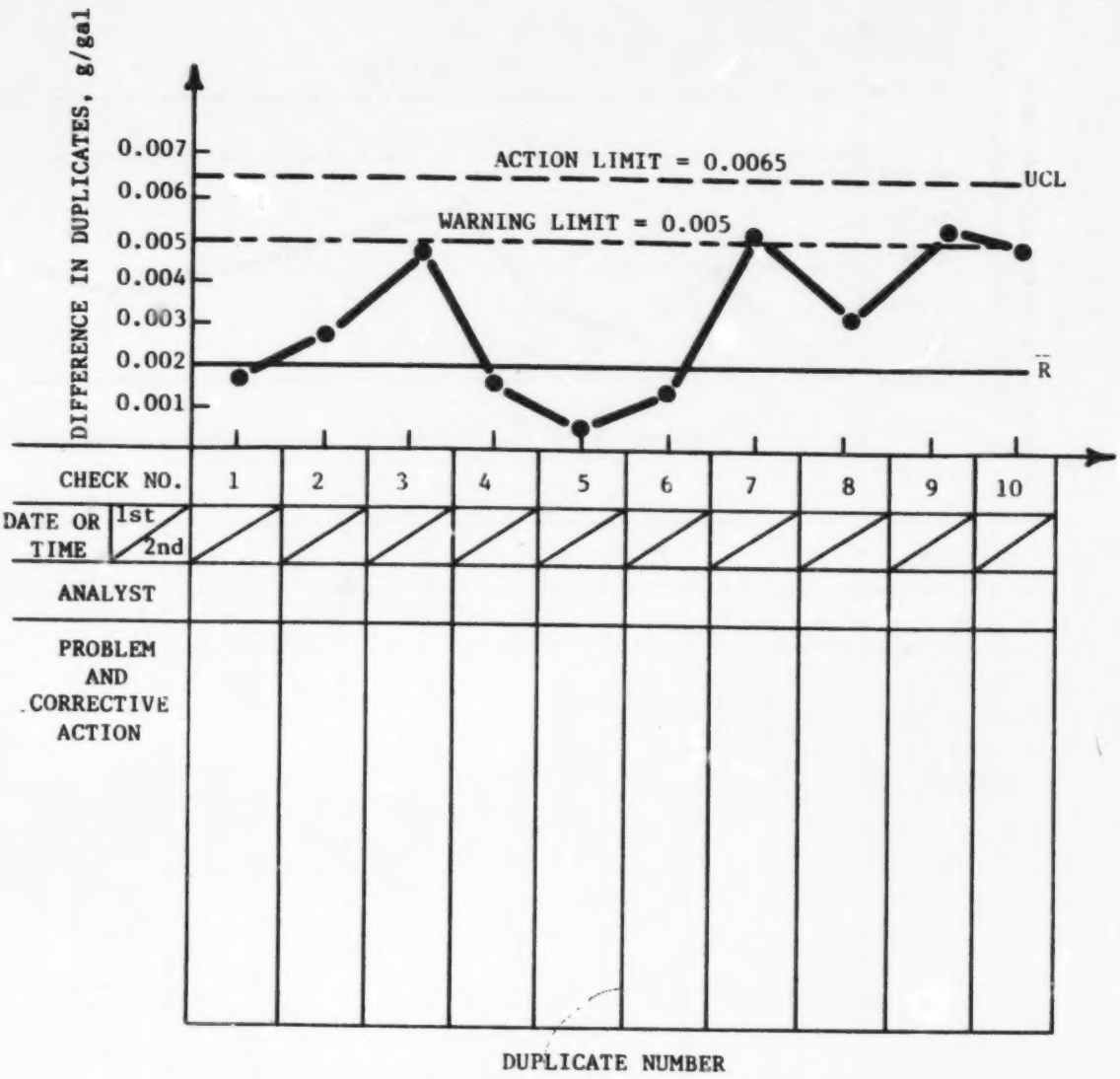


Figure 8. Sample control chart for duplicate measurements of gasoline samples.

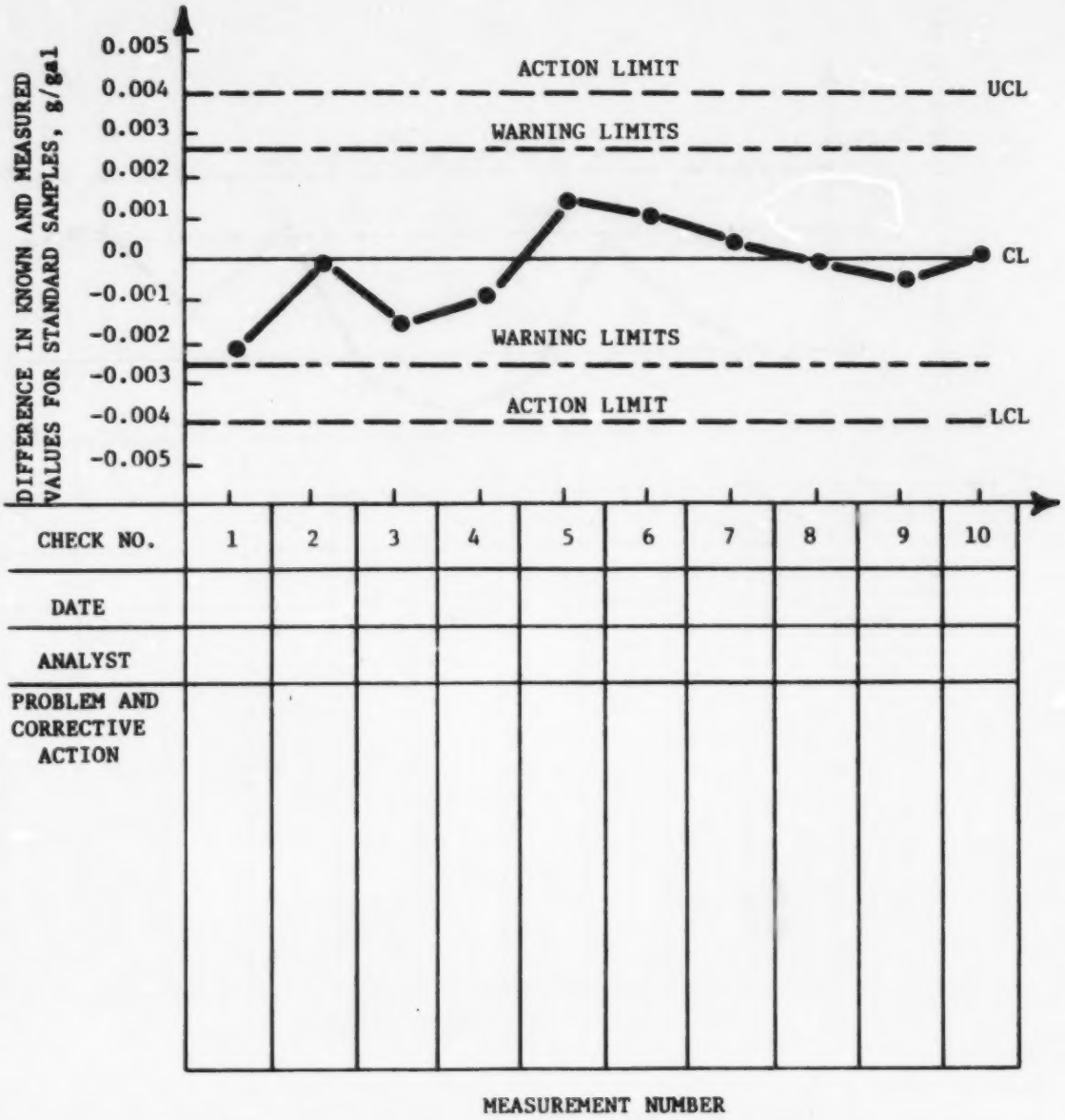


Figure 9. Sample control chart for the measurement of working standard samples.

value and the known value of standard samples. The UCL is taken as the 3-sigma value, and it is assumed that three standard deviations is 0.004 g Pb/gal. As each standard is measured, the difference should be computed and plotted on the graph. Each point is connected to the previously plotted point with a straight line. Corrective action, such as preparing new standards and/or recalibrating the spectrometer, should be taken anytime:

1. One point falls outside the action limits.
2. Two out of three points fall between the warning and action lines, and
3. Seven consecutive points fall on the same side of the average or zero line.

Analysis of gasoline samples should not be attempted until a standard sample (i.e., a sample prepared from the standard lead solution) can be measured to within $\pm$0.004 g Pb/gal.

## 3.3 INDEPENDENT PERFORMANCE AUDIT

If implemented properly, an independent audit can be used to evaluate the total measurement process through the use of standard reference samples (SRS). An SRS is defined as a gasoline sample whose lead content is accurately known (preferably NBS certified) to the auditors, but unknown to the analyst being audited. Results from an audit provide an independent assessment of data quality by providing a means of estimating the precision and bias of the reported results. If SRS's are not feasible, then other NBS-certified lead samples (e.g., lead in iso-octane), even though it will be obvious to the analyst that they are special samples, can be used. The results may not estimate the true variability of the measurement method because of the recognizible special samples.

### 3.3.1 Procedure for Performing a Quality Audit

The individual or organization responsible for performing the audit should obtain a supply of gasoline samples with known lead concentrations. Samples should be placed in sample containers identical to the containers used in the field. If possible the SRS should not be distinguishable from regular field samples. These reference samples should be shipped or delivered to the analysis laboratory in the same manner that is used for field samples.

### 3.3.2 Frequency of Audit

The optimum frequency of audit is a function of certain costs and the desired level of confidence in the data quality assessment. Also, another consideration would have to be the quality of the data presently being reported. The repeatability of this method appears small enough to indicate that within-laboratory precision of the method will not be a big problem. However, reproducibility or between-laboratory biases could be important to the accuracy (bias) of the reported data.

Initially an auditing level of once every 20 samples or once for every measurement cycle if less than 20 samples are to be analyzed is recommended. If the data for the first audit period (calendar quarter) indicate that only good quality data are being reported, the auditing level could be reduced. However, the lower the audit level, the higher becomes the risk of declaring good data bad. The risk of declaring bad data good is constant for all audit levels for the proposed sampling plan.

## 3.4 DATA QUALITY ASSESSMENT

Two aspects of data quality assessment are considered in this section. The first considers a means of estimating the precision and accuracy of the reported data, e.g., reporting the bias, if any, and the standard deviation associated with the measurements. The second consideration is that of testing the data quality against given standards using sampling by variables. For example, lower and upper limits, L and U, may be selected to include a large percentage of the measurements and outside of which it is desired to control the percentage of measurements to, say, less than 10 percent. If the data quality is not consistent with these limits, L and U, then action is taken to correct the possible deficiency as quickly as possible and to correct the previous data when possible and/or feasible.

### 3.4.1 Estimating the Precision/Accuracy of the Reported Data

This section will indicate how the audit data collected in accordance with the procedure described in Section 3.3.1 will be utilized to estimate the precision and accuracy of the measure of interest. Similar techniques can also be used by a specific firm or laboratory to assess their or its own measurements. The audit data collected as a result of following the

procedures in the previous section are the measured and known values of $P_c$ and the difference:

$$d_j = C_{Pb_j} - C'_{Pb_j}$$

where

$C_{Pb_j}$ = measured value of lead in the reference sample, g Pb/gal,

$C'_{Pb_j}$ = known value of lead in the reference sample, g Pb/gal, and

= the audit number, j = 1, . . . n.

Let the mean and standard deviation of the differences $d_j$, j = 1, . . . n audits be denoted by $\bar{d}$ and $s_d$, respectively. Thus,

$$\bar{d} = \sum_{j=1}^{n} d_j/n,$$

and

$$s_d = \left[ \sum_{j=1}^{n} (d_j - \bar{d})^2/(n-1) \right]^{1/2}$$

3.4.2 Statistical Tests

The mean $\bar{d}$ is an estimate of the relative bias in the measurements (i.e., relative to the known or accepted value). Assuming the audit value to be unbiased, the existence of a bias in the laboratory data can be checked by the appropriate t-test, i.e.,

$$t_{n-1} = \frac{\bar{d} - 0}{s_d/\sqrt{n}} .$$

See reference 12 for a discussion of the t-test. If t is significantly large in absolute values, i.e., greater than the tabulated value of t with n - 1 degrees of freedom, which is exceeded by chance only 5 percent of the time, then the bias is considered to be real and some check should be made for a possible cause of the bias. If t is not significantly large, then the bias should be considered zero or negligible. However, its calculated value will be reported with the laboratory data for that audit period.

The standard deviation, $s_d$, is a function of both the standard deviation of the laboratory measurements and of precision with which the reference-sample value is known. Assuming the reference-sample values are known with much greater precision than the laboratory measurements, then the calculated $s_d$ is an estimate of the standard deviation of the laboratory measurement. Table 3 contains an example calculation of $\bar{d}$ and $s_d$, starting with the differences for a sample size of n = 12.

The calculated standard deviation can then be utilized to check the reasonableness of the assumption made in subsection 3.1.2 concerning $\sigma\{C_{Pb}\} = \sigma_R = 0.0036$ g Pb/gal, under reproducibility conditions. The calculated standard deviation, $s_d$, may be directly checked against the assumed value, $\sigma_R$, by using the statistical test procedure

$$\frac{\chi^2}{f} = \frac{s_d^2}{\sigma^2\{C_{Pb}\}},$$

where $\chi^2/f$ is the value of a random variable having the chi-square distribution with f = n - 1 degrees of freedom. If $\chi^2/f$ is larger than the tabulated value exceeded only 5 percent of the time, then it would be concluded that the test procedure is yielding results with more variability than is acceptable, due to some assignable cause of large variation.

The measured values should be reported along with the estimate bias, $\bar{d}$, standard deviation, $s_d$, the number of audits, n, and the total number of determination periods (number of days analyses were performed) N, sample ($n \leq N$). Estimates, i.e., $s_d$ and $\bar{d}$, which are significantly different from the assumed population parameters should be identified on the data sheet. For example, based on the data of table 3, if the analyst reported a value of $C_{Pb} = 0.05$ g Pb/gal for one of the N field tests not audited, then that measurement would be reported as

1. Measured value, $C_{Pb} = 0.05$ g Pb/gal
2. Calculated bias, $\bar{d} = \hat{\tau} = -0.00075$ g Pb/gal
3. Calculated standard deviation, $\hat{\sigma}_R\{C_{Pb}\} = s_d = 0.0025$ g Pb/gal
4. Auditing level, n = 12, N = 65 (N = 5 days per week x 13 weeks per quarter).

From the above data, users of the data can calculate confidence limits appropriate to what the data are to be used for.

Table 3. Computation of mean difference, $\bar{d}$, and standard deviation of differences, $s_d$

| General formulas $d = C_{Pb_j} - C'_{Pb_j}$ | | Specific example Data (g/gal) | |
|---|---|---|---|
| $d_1$ | $d_1^2$ | -0.005 | 0.000025 |
| $d_2$ | $d_2^2$ | -0.002 | 0.000004 |
| $d_3$ | $d_3^2$ | 0.000 | 0.000000 |
| $d_4$ | $d_4^2$ | -0.003 | 0.000009 |
| $d_5$ | $d_5^2$ | -0.006 | 0.000036 |
| $d_6$ | $d_6^2$ | 0.001 | 0.000001 |
| $d_7$ | $d_7^2$ | 0.002 | 0.000004 |
| $d_8$ | $d_8^2$ | 0.003 | 0.000009 |
| $d_9$ | $d_9^2$ | 0.004 | 0.000016 |
| $d_{10}$ | $d_{10}^2$ | 0.001 | 0.000001 |
| $d_{11}$ | $d_{11}^2$ | -0.003 | 0.000009 |
| $d_{12}$ | $d_{12}^2$ | 0.000 | 0.000000 |
| $\Sigma d_j$ | $\Sigma d_j^2$ | -0.008 | 0.000114 |
| $\bar{d} = \Sigma d_j / n$ | | $\bar{d} = -0.0007$ | |
| $s_d^2 = \frac{\Sigma d_j^2 - (\Sigma d_j)^2/n}{n-1}$ | | $s_d^2 = 0.0000065$ | |
| $s_d = \sqrt{s_d^2}$ | | $s_d = 0.0025$ g/gal | |

The t-test and $\chi^2$-test described above are used to check on the biases and standard deviations separately. In order to check on the overall data quality as measured by the percent of measurement deviations outside prescribed limits, it is necessary to use the approach described below.

### 3.4.3 Sampling by Variables

Because the lot size (i.e., the number of determination periods during a particular period, normally a calendar quarter) is small, N < 150 (estimated), and consequently, the sample size is small on the order of n = 7 to 13, it is important to consider a sampling by variables approach to assess the data quality with respect to prescribed limits. That is, it is desired to make as much use of the data as possible. In the variables approach, the means and standard deviations of the sample of n audits are used in making a decision concerning the data quality.

Some background concerning the assumptions and the methodology is repeated below for convenience. However, one is referred to one of a number of publications having information on sampling by variables; e.g., see references 12-16. The discussion below will be given in regard to the specific problem herein, which has some unique features as compared with the usual variable sampling plans.

The difference between the analyst-measured and the known value of $C_{Pb}$ is designated as $d_j$, and the mean difference over n audits by $\bar{d}$, that is,

$$\bar{d} = \frac{1}{n} \sum_{j=1}^{n} (C_{Pb_j} - C'_{Pb_j}).$$

Theoretically, $C_{Pb_j}$ and $C'_{Pb_j}$ should be measures of the same lead concentration, and their difference should have a mean of zero on the average. In addition, their differences should have a standard deviation approximately equal to that associated with measurements of $C_{Pb_j}$ separately.

Assuming three standard deviation limits (using the assumed $\sigma\{C_{Pb}\}$ = 0.0036 g Pb/gal as derived in the variance analysis of subsection 3.1.2), the values -3(0.0036) ≈ -0.011 g Pb/gal and 3(0.0036) ≈ 0.011 g Pb/gal define lower and upper limits, L and U, respectively, outside of which it is desired to control the proportion of differences, $d_j$. Following the method

given in reference 13, a procedure for applying the variables sampling plan is described below. Figures 10 and 11 illustrate examples of satisfactory and unsatisfactory data quality with respect to the prescribed limits L and U.

The variables sampling plan requires the sample mean difference, $\bar{d}$; the standard deviation of these differences, $s_d$; and a constant, k, which is determined by the value of p, the proportion of the differences outside the limits of L and U. For example, if it is desired to control at 0.10 the probability of not detecting lots with data quality p equal to 0.10 (or 10 percent of the individual differences outside L and U) and if the sample size n = 12, then the value of k can be obtained from Table II of reference 13. The values of $\bar{d}$ and $s_d$ are computed in the usual manner; see table 3 for formulas and a specific example. Given the above information, the test procedure is applied and subsequent action is taken in accordance with the following criteria:

1. If both of the following conditions are satisfied:

$$\bar{d} - k\, s_d \geq L = -0.011 \text{ g Pb/gal}$$

$$\bar{d} + k\, s_d \leq U = 0.011 \text{ g Pb/gal}$$

the individual differences are considered to be consistent with the prescribed data quality limits and no corrective action is required.

2. If one or both of these inequalities is violated, possible deficiencies exist in the measurement process as carried out for that particular lot (group) of determination periods. These deficiencies should be identified and corrected as soon as possible to prevent future measurements of unacceptable quality. Data corrections should be made when possible, i.e., if a quantitative basis is determined for correction.

Table 4 contains a few selected values of n, p, and k for convenient reference.

Using the values of $\bar{d}$ and $s_d$ in table 3, k = 2.045 for a sample size of n = 12, and p = 0.10 (table 4), the test criteria can be checked; i.e.,

$\bar{d} - k\, s_d = -0.00075 - (2.045)\ (0.0025) = -0.0059 > L = -0.011$ g Pb/gal

$\bar{d} + k\, s_d = -0.00075 + (2.045)\ (0.0025) = 0.0044 < U = 0.011$ g Pb/gal

Therefore, both inequalities are satisfied; hence, the data are consistent

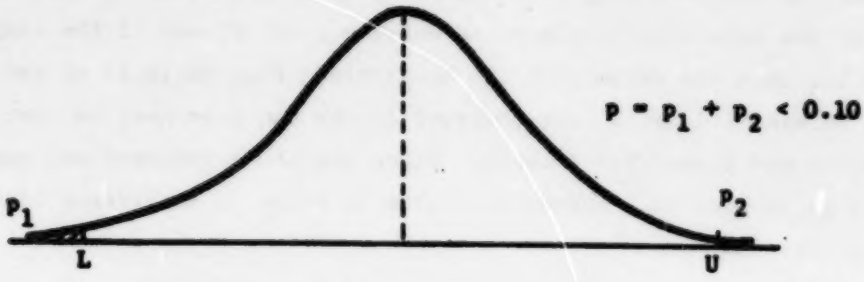


Figure 10. Example illustrating $p < 0.10$ and satisfactory data quality.

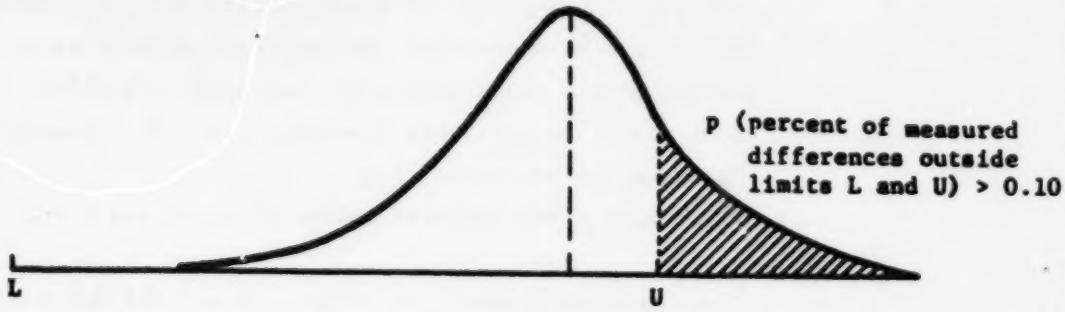


Figure 11. Example illustrating $p < 0.10$ and unsatisfactory data quality.

with the limits. The laboratory responsible for generating these data should be notified that its quality control activities are satisfactory. Even if the limits had been exceeded, the calendar quarter of data or a portion of that quarter of data should be invalidated only if one or more of the reported measurements approached, within measurement error, or exceeded, the standard.

The above plan provides a 90-percent probability of detecting lots with 10 percent or more defects (i.e., deviations falling outside the designated limits L and U).

Table 4. Sample plan constants, k for P{not detecting a lot with proportion p outside limits L and U} $\leq$ 0.1

| Sample Size n | k(p = 0.2) | k(p = 0.1) |
|---|---|---|
| 3 | 3.039 | 4.258 |
| 5 | 1.976 | 2.742 |
| 7 | 1.721 | 2.334 |
| 10 | 1.595 | 2.112 |
| 12 | 1.550 | 2.045 |
| 13 | 1.533 | 2.02 |
| 14 | 1.519 | 1.999 |
| 15 | 1.506 | 1.981 |

## SECTION IV REFERENCES


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# APPENDIX A — TEST FOR THE DETERMINATION OF LEAD IN GASOLINE

### TEST FOR LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROMETRY

1. *Scope.* 1.1 This method covers the determination of the total lead content of gasoline within the concentration range of 0.010 to 0.10 g of lead/U.S. gal. The method compensates for variations in gasoline composition and is independent of lead alkyl type.

2. *Summary of method.* 2.1 The gasoline sample is diluted with methyl isobutyl ketone and the alkyl lead compounds are stabilized by reaction with iodine and a quarternary ammonium salt. The lead content of the sample is determined by atomic absorption flame spectrometry at 2833 A, using standards prepared from reagent grade lead chloride. By the use of this treatment, all alkyl lead compounds give identical response.

3. *Apparatus.* 3.1 Atomic Absorption Spectometer, capable of scale expansion and nebuliser adjustment, and equipped with a slot burner and premix chamber for use with an air-acetylene flame.

3.2 Volumetric Flasks, 50-ml, 100-ml, 250-ml, and one litre sizes.

3.3 Pipets, 2-ml, 5-ml, 10-ml, 20-ml, and 50-ml sizes.

3.4 Micropipet, 100-µl, Eppendorf type or equivalent.

4. *Reagents.* 4.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

4.3 Aliquat 336 (tricapryl methyl ammonium chloride).

4.4 Aliquat 336/MIBK Solution (10 percent v/v)—Dissolve and dilute 100 ml (88.0 g) of Aliquat 336 with MIBK to one liter.

4.5 Aliquat 336/MIBK Solution (1 percent v/v)—Dissolve and dilute 10 ml (8.8 g) of Aliquat 336 with MIBK to one liter.

4.6 Iodine Solution—Dissolve and dilute 8.0 g iodine crystals with Toluene to 100 ml.

4.7 Lead Chloride.

4.8 Lead-Sterile Gasoline—Gasoline containing less than 0.005 g Pb/gal.

4.9 Lead, Standard Solution (5.0 g Pb/gal)—Dissolve 0.4433 g of lead chloride ($PbCl_2$) previously dried at 105°C for 3 h in about 200 ml of 10 percent Aliquat 336 MIBK solution in a 250-ml volumetric flask. Dilute to the mark with the 10 percent Aliquat solution, mix, and store in a brown bottle having a polyethylene-lined cap. This solution contains 1.321 ag Pb/ml, which is equivalent to 5.0 g Pb/gal.

4.10 Lead, Standard Solution (1.0 g Pb/gal)—By means of a pipet, accurately transfer 50.0 ml of the 5.0 g Pb/gal solution to a 250-ml volumetric flask, dilute to volume with 1 percent Aliquat/MIBK solution. Store in a brown bottle having a polyethylene-lined cap.

4.11 Lead, Standard Solutions (0.02, 0.05, and 0.10 g Pb/gal)—Transfer accurately by means of pipets 2.0, 5.0, and 10.0 ml of the 1.0-g Pb/gal solution to 100-ml volumetric flasks; add 5.0 ml of 1 percent Aliquat 336 solution to each flask; dilute to the mark with MIBK. Mix well and store in bottles having polyethylene-lined caps.

4.12 Methyl Isobutyl Ketone (MIBK). (4-methyl-2-pentanone).

5. *Calibration.* 5.1 Preparation of Working Standards—Prepare three working standards and a blank using the 0.02, 0.05, and 0.10-g Pb/gal standard lead solutions described in 4.11.

5.1.1 To each of four 50-ml volumetric flasks containing 30 ml of MIBK, add 5.0 ml of low lead standard solution and 5.0 ml of lead-free gasoline. In the case of the blank, add only 5.0 ml of lead-free gasoline.

5.1.2 Add immediately 0.1 ml of iodine/toluene solution by means of the 100-µl Eppendorf pipet. Mix well.[1]

5.1.3 Add 5 ml of 1 percent Aliquat 336 solution and mix.

5.1.4 Dilute to volume with MIBK and mix well.

5.2 Preparation of Instrument—Optimize the atomic absorption equipment for lead at 2833 A. Using the reagent blank, adjust the gas mixture and the sample aspiration rate to obtain an oxidizing flame.

5.2.1 Aspirate the 0.1-g Pb/gal working standard and adjust the burner position to give maximum response. Some instruments require the use of scale expansion to produce a reading of 0.150 to 0.170 for this standard.

5.2.2 Aspirate the reagent blank to zero the instrument and check the absorbances of the three working standards for linearity.

6. *Procedure.* 6.1 To a 50 ml volumetric flask containing 30 ml MIBK, add 5.0 ml of gasoline sample and mix.[2]

6.1.1 Add 0.10 ml (100 µl) of iodine/toluene solution and allow the mixture to react about 1 min.[1]

6.1.2 Add 5.0 ml of 1 percent Aliquot 336/MIBK solution and mix.

6.1.3 Dilute to volume with MIBK and mix.

6.2 Aspirate the samples and working standards and record the absorbance values with frequent checks of the zero.

7. *Calculations.* 7.1 Plot the absorbance values versus concentration represented by the working standards and read the concentrations of the samples from the graph.

8. *Precision.* 8.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

8.1.1 Repeatability—Duplicate results by the same operator should be considered suspect if they differ by more than 0.005 g/gal.

8.1.2 Reproductibility—The results submitted by each of two laboratories should not be considered suspect unless the two results differ by more than 0.01 g/gal.

[FR Doc.74-15449 Filed 7-5-74,8:45 am]

# APPENDIX B GLOSSARY OF SYMBOLS

| SYMBOL | DEFINITION |
|---|---|
| A | Absorbance |
| Å | Angstrom |
| cm | Centimeter |
| gal | Gallon |
| g | Gram |
| I | Transmitted Light |
| $I^{\circ}$ | Incident Light |
| µℓ | Microliter |
| mℓ | Milliter |
| Pb | Lead |
| ℓ | Liter |
| / | Per |
| nm | Nanometer |
| T | Transmittance |
| µ | Micron |
| N | Lot size--i.e., the number of determination periods to be treated as a group |
| n | Sample size for the quality audit (section 3.3) |
| r | Repeatability of the measurement method at the 95-percent confidence level |
| $\sigma\{X\}$ | Assumed standard deviation of the parameter X (population standard deviation) |
| $\mu_X$ | Assumed mean value of the parameter X (population mean) |
| $\bar{X}$ | Computed average of a finite sample of measurements (sample mean) |
| R | Reproducibility of the measurement method (section 3.0) |
| R | Range; i.e., the difference in duplicate |
| $\bar{R}$ | Average range or difference for duplicate results (fig. 6) |

## APPENDIX B GLOSSARY OF SYMBOLS—CONTINUED

| SYMBOL | DEFINITION |
|---|---|
| $d_j$ | The difference in the audit value and the measured value arrived at by the analyst for the jth audit |
| $\bar{d}$ | Mean difference between known and measured values of reference samples for n audits |
| $s_d$ | Computed standard deviation of difference between known and measured values |
| P | Percent of measurements outside specified limits L and U (section 3.4) |
| k | Constant used in sampling variables (section 3.4) |
| p{Y} | Probability of event Y occurring |
| $\sigma_r$ | Repeatability standard deviation |
| $\sigma_R$ | Reproducibility standard deviation |
| $t_{n-1}$ | Statistic used to determine if the sample bias, $\bar{d}$, is significantly different from zero (t-test) |
| $\frac{\chi^2}{f}$ | Statistic used to determine if the sample variance, $s^2$, is significantly different from the assumed variance, $\sigma^2$, of the parent distribution (chi-square test) |
| L | Lower quality limit used in sampling by variables |
| U | Upper quality limit used in sampling by variables |
| CL | Center line of a quality control chart |
| LCL | Lower control limit of a quality control chart |
| UCL | Upper control limit of a quality control chart |
| $C'_{Pb}$ | Measured lead in a gasoline sample in g/gal |
| | The known concentration of lead in reference sample, g/gal |
| $C_{Pb}$ | The average of several measurements on the same or identical samples (eq. 1) |

## APPENDIX C GLOSSARY OF TERMS

The following glossary lists and defines the terms as used in this document.

| | |
|---|---|
| **Absorbance** | The logarithm to the base 10 of the reciprocal of transmittance. |
| **Accuracy** | A measure of the error of a process expressed as a comparison between the measured value and the true value. |
| **Bias** | The systematic or nonrandom component of system error. |
| **Chain of Custody Label** | The seal placed on the container which contains the gasoline sample from the test station. |
| **Determination Method** | A set of procedures for making a determination. |
| **Determination Process** | The process of making a determination including method, personnel, equipment, and environmental conditions. |
| **Lot** | A specified number of objects to be treated as a group. |
| **Population** | A very large number of like objects (i.e., measurements, checks, etc.) from which the true mean and standard deviation can be deduced with a high degree of accuracy. |
| **Precision** | The degree of variation among measurements on a homogeneous material under controlled conditions, and usually expressed as a standard deviation or as a coefficient of variation. |
| **Quality Audit** | A management tool for independently assessing data quality. |
| **Quality Control Check** | Checks made by the operator on certain items of equipment and procedures to assure data of good quality. |
| **Quality Control Sample** | Sample whose Pb concentration is known to the analyst. |
| **Repeatability** | The value below which the absolute difference between duplicate results, i.e., two measurements made on the same sample by the same analyst in the same laboratory using the same equipment over a short interval of time, may be expected to fall with a 95 percent probability. |

## APPENDIX C GLOSSARY OF TERMS—CONTINUED

| | |
|---|---|
| Reproducibility | The value below which the absolute difference between two measurements made on the same sample by different analysts in different laboratories using different equipment may be expected to fall with 95 percent probability. |
| Sample | Objects drawn usually at random from the lot for checking. |
| Standard Reference Sample (SRS) | Certified sample submitted to laboratory for quality control check as part of an independent performance audit. |
| Transmittance | Transmittance is the ratio of the transmitted light to the incident light. |
| Working Standard Sample | Sample prepared by the analyst from the standard lead solution to check the lead calibration curve. |

## APPENDIX D CONVERSION FACTORS

| TO CONVERT FROM | TO | MULTIPLY BY |
|---|---|---|
| Nanometer (nm) | Micron (μ) | 0.001 |
| | Angstom (Å) | 0.1 |
| | Centimeter (cm) | $10^{-7}$ |
| Gal | Liter (ℓ) | 3.785 |
| Transmittance (T) | Absorbance (A) | $T = 10^{-A}$ |